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Sulfated tungstate: An efficient catalyst for synthesis of thioamides *via* Kindler reaction

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ABSTRACT

New application of sulfated tungstate, a mildly acidic solid inorganic acid, as reusable heterogeneous catalyst for efficient Kindler reaction, a three component reactions of aldehydes, amines and sulfur, for synthesis of thioamides is discussed.

1. Introduction

Appreciating the campaign for green chemistry and continuing pressure on limiting resources, chemical sustainability has become a focal point of research. One of the approaches toward chemical sustainability can be through development of catalytic methods with environmentally benign, easy to recover and reusable catalyst. Recently our group, working toward this goal, has synthesized and well characterized sulfated tungstate [1], as green, reusable, heterogeneous, mildly acidic catalyst and demonstrated its effectiveness in amide bond formation [1,2], Biginelli [3], Willgerodt–Kindler [4] and Strecker [5] reactions. On the same track it was thought that sulfated tungstate might catalyze Kindler reaction [6], a three component reaction of aldehyde, amine and sulfur satisfactorily conducted under acid catalyzed conditions, for synthesis of thioamides and indeed this was observed. Thioamides are an important class of compounds and show broad spectrum of bioactivity such as antibacterial, antimycobacterial, antiulcerative, fungicidal, anticancer and spasmolytic [7–13]. Ethionamide and prothionamide are two examples of thioamide containing drugs which are in clinical use for treatment tuberculosis. Thioamides find wide applications as intermediates in synthesis of five and six membered heterocycles [14–17], and active pharmaceutical ingredients such as fentiazac, fenclosic acid and febuxostate [18,19]. A good number of preparative methods are available in literature for synthesis of thioamides and the most frequently used methods are based on thionation of amides. Thionation of amides is affected using thionating reagents, such as P_4S_{10} [20–25], diethylthiocarbamoyl chloride [26], ethylaluminum sulfide [27], boron sulfide [28,29], use of $PSCl_3/H_2O/Et_3N$ system [30] and Lawesson's reagent [31]. Thionation of amides is also achieved by activation of amides with electrophilic reagents, such as oxalyl chloride and phosphorousoxychloride and benzyltriethylammonium tetrathiomolybdate [32] and hexamethyldisilathiane [33], followed by treatment with thionating agents. These approaches suffer from drawbacks like toxicity of reagents, bad odor, corrosive nature, explosive properties, formation of uncontrolled by-products with lower yields. In the past few years, improved reagents such as fluorous based Lawesson's reagents [34], encapsulated P_4S_{10} [35] and polymer supported thionating agents [36] have been developed to address some of these drawbacks. Willgerodt–Kindler [37,38] and Kindler reactions [6], classical three component reactions of ketones/aldehydes, amines and sulfur, are direct oxidative sulfurization methods for thioamide synthesis. Kindler reaction, where the three components are aldehyde, primary/secondary amines, ammonia or ammonium salt and sulfur, has potential for wide applicability for synthesis of diverse set of useful thioamides in one pot with high atom economy and with water as the only condensation by-product, because a large

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